

(19) Japanese Patent Office

(11) Publication Number  
11-208098 (208098-1999)

**(12) THE LAID-OPEN PATENT GAZETTE (A)**

(43) Publication date 3<sup>rd</sup> August 1999

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(51) Int.Cl.<sup>6</sup> Identification code

FI

B41M 5/00

B41M 5/00

B

Request for Examination Not Received

Number of Claims 4 OL (Total 14 sheets)

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(21) Application number

10-14607 (14607-1998)

(22) Application date

27<sup>th</sup> January 1998

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(54) [Title of the Invention]

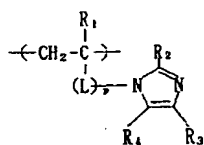
An image-recording medium

(57) [Abstract]

[Problem] To provide an image-recording medium where the ink drying rate is high, the image quality outstanding and the light fastness excellent.

[Resolution Means] An image-recording medium where, in an image-recording medium having two or more coating layers on a substrate, dye-receptive polymer represented by general formula (I) and one or more types of silica pigment are incorporated into the same layer. (In the formula,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  each independently represent a hydrogen atom or an alkyl group, which may be linear or branched; L represents a divalent connecting group; and p represents 0 or 1.)

[Chem. 1]



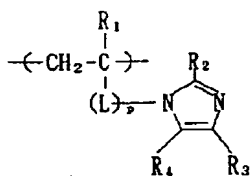
General formula (I)

## [Scope of Claims]

**[Claim 1]** An inkjet image-recording medium which is characterized in that, in an image-recording medium having two or more coating layers on a substrate, dye-receptive polymer represented by general formula (I) and one or more types of silica pigment are incorporated into the same layer.

General formula (I)

[Chem.1]



(In the formula, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each independently represent a hydrogen atom or an alkyl group, which may be linear or branched; L represents a divalent connecting group; and p represents 0 or 1.)

**[Claim 2]** An inkjet image-recording medium according to Claim 1 which is characterized in that, of the two or more coating layers, the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment are contained in a lower layer.

**[Claim 3]** An inkjet image-recording medium according to Claim 1 or Claim 2 which is characterized in that, of the two or more coating layers, the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment are contained in a lower layer and, furthermore, dye-receptive polymer represented by general formula (I) is contained in an upper layer.

**[Claim 4]** An inkjet image-recording medium according to Claim 1 or Claim 2 which is characterized in that, of the two or more coating layers, the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment are contained in a lower layer and, furthermore, one or more types of inorganic pigment are contained in an upper layer.

**[Detailed Description of the Invention]**

[0001]

[Technical Field of the Invention] The present invention relates to an image-recording medium which is outstanding in terms of image quality and outstanding in terms of light fastness. Furthermore, the present invention relates to a recording medium which is outstanding in its photographic image quality in inkjet recording or the like.

[0002]

[Prior Art] In recent years, along with the popularization of the personal computer, there has been a rapid spread of printers such as inkjet printers. Moreover, with the popularization of photographic image scanners, photo CDs and digital cameras, the demand for printing systems for printing digitalized photographic images has been increasing rapidly. In particular, the spread of simple and inexpensive inkjet printers has been marked, and demands in terms of their image quality have also been increasing year by year.

[0003] As a recording medium with a high ink drying rate, there has been disclosed in JP-A-8-230309 and JP-A-6-183134 for example a recording medium employing silica pigment. Again, in JP-A-3-281383, JP-A-4-267180 and JP-A-5-24335, a recording medium employing alumina pigment is disclosed. In these, the recording layer is made porous, so ink absorption is improved and the drying rate is rapid. However, since in these examples the ink is adsorbed onto a silica pigment or onto an alumina pigment, which are inorganic pigments, there is the problem that the light fastness is markedly impaired. Hence, there is a considerable desire for a recording medium where the ink drying rate is high, the image quality outstanding and the light fastness excellent.

[0004]

[Problem to be Resolved by the Invention] The objective of the present invention lies in providing an image-recording medium which has a high ink drying rate, which is outstanding in its image quality and which has excellent light fastness. A further aim is to provide an image-recording medium where high image quality and light fastness can be obtained using printers which print digital image data such as an inkjet printer, in particular an inkjet printer of enhanced performance and rapid printing rate, or an inkjet printer where the image quality is improved by discharge of numerous ink droplets of low concentration.

[0005]

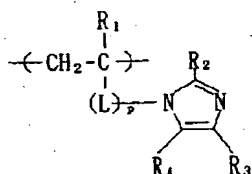
[Means for Resolving the Problem] The aforesaid objectives of the present invention are realized by the following means.

(1) An inkjet image-recording medium which is characterized in that, in an image-recording medium having two or more coating layers on a substrate, dye-receptive polymer represented by general formula (I) and one or more types of silica pigment are incorporated into the same layer.

General formula (I)

[0006]

[Chem.2]



[0007] (In the formula, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each independently represent a hydrogen atom or an alkyl group, which may be linear or branched; L represents a divalent connecting group; and p represents 0 or 1.)

(2) An inkjet image-recording medium as described in (1) which is characterized in that, of the two or more coating layers, the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment are contained in a lower layer.

(3) An inkjet image-recording medium as described in (1) or (2) which is characterized in that, of the two or more coating layers, the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment are contained in a lower layer and, furthermore, dye-receptive polymer represented by general formula (I) is contained in an upper layer.

(4) An inkjet image-recording medium as described in (1) or (2) which is characterized in that, of the two or more coating layers, the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment are contained in a lower layer and, furthermore, one or more types of inorganic pigment are contained in an upper layer.

[0008]

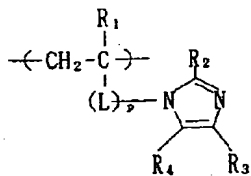
[Mode of Practising the Invention] In the present invention, by incorporating dye-receptive polymer represented by general formula (I) and one or more types of silica pigment in the same layer, it has been discovered that, surprisingly, these produce a structure and an outstanding porous layer is obtained. Hence, a synergistic effect in terms of enhancing the ink absorption rate and the dye-receptive strength is manifested to a degree which cannot be expected in the case where these are used on their own, and it is possible to provide an inkjet image-recording medium with extremely outstanding image quality and excellent light fastness.

[0009] Below, the present invention is explained in detail. The present invention is an inkjet image-recording medium having two or more coating layers on a substrate, and it is characterized in that dye-receptive polymer represented by general formula (I) and one or more types of inorganic {sic} pigment are contained in the same coating layer.

General formula (I)

[0010]

[Chem. 3]

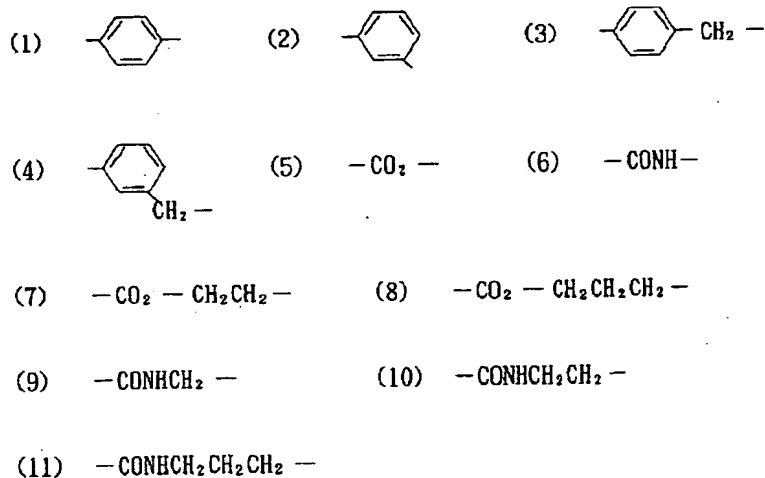


[0011] In the formula, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each independently represent a hydrogen atom or an alkyl group, which may be linear or branched. L represents a divalent connecting group. p represents 0 or 1. In particular, it is preferred that R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each independently represent a hydrogen atom or a lower alkyl group such as the methyl group, ethyl group, n-propyl group, n-butyl group, n-amyl group or n-hexyl group, and it is particularly preferred that they represent a hydrogen atom or a methyl or ethyl group. L represents a divalent connecting group having from 1 to around 20 carbon atoms, examples being alkylene, phenylene or arylene groups, etc. Specific examples of these divalent groups are shown below.

[0012]

[Chem. 4]

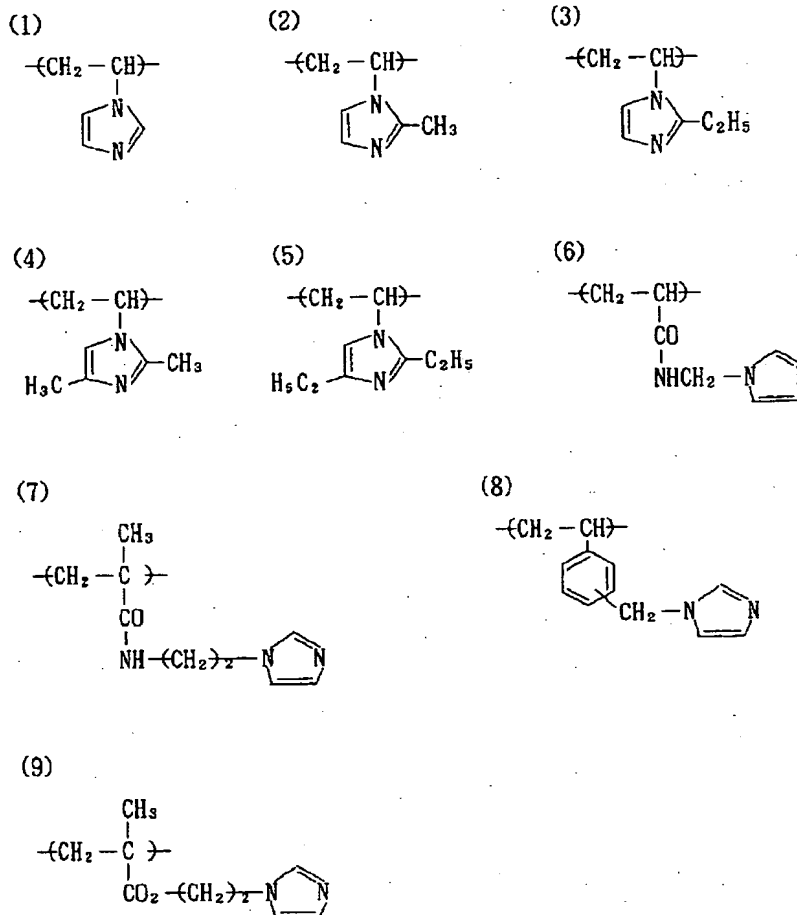




[0013] Preferred specific examples of the monomer units in the dye-receptive polymer represented by general formula (I) of the present invention are shown below. However, the present invention is not to be restricted to these.

[0014]

[Chem. 5]

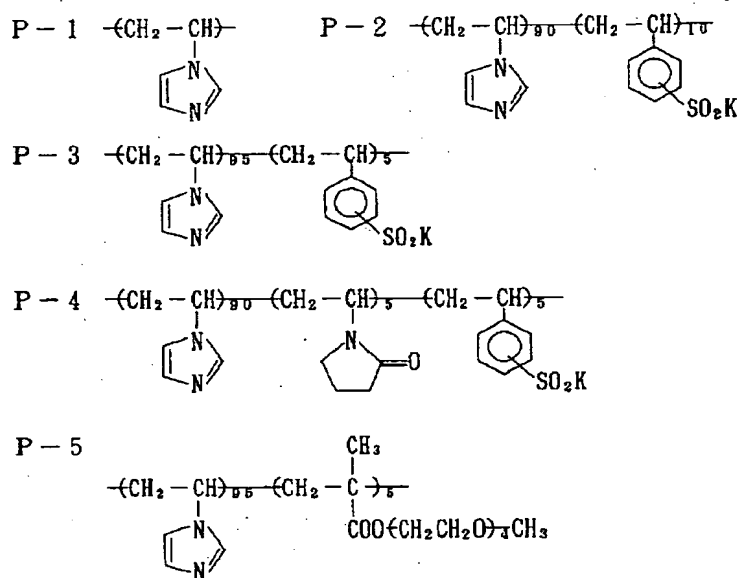


[0015] The dye-receptive polymer which can be used in the present invention may also include monomer units other than monomer units represented by general formula (I), and the preferred such monomer units are pyrrolidones, acrylate esters (such as n-butyl acrylate), methacrylate esters (such as n-butyl methacrylate), acrylamides (such as diacetone acrylamide), methacrylamides (such as n-butyl methacrylamide) and styrenes (such as styrenesulfinic acid). Furthermore, there may also be included the co-monomers described in JP-A-59-169042 and JP-A-62-244036. Two or more of these monomer units may be used. The molecular weight of the dye-receptive polymer which can be used in the present invention is preferably in the range  $5 \times 10^3$  to  $1 \times 10^7$ .

If the molecular weight is too low, then the polymer may readily migrate, while if it is too high then impediments may arise in the coating thereof. Below, specific examples of preferred dye-receptive polymers used in the present invention are provided but the present invention is not restricted to these. Furthermore, two or more types may be jointly used.

[0016]

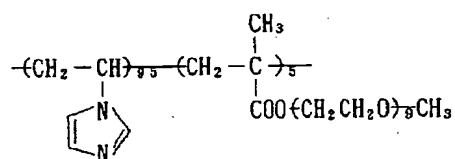
[Chem. 6]



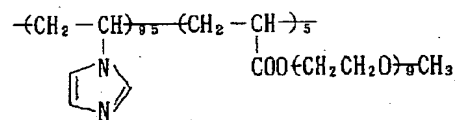
[0017]

[Chem. 7]

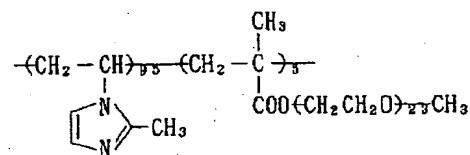
P - 6



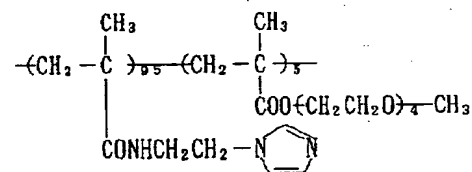
P - 7



P - 8



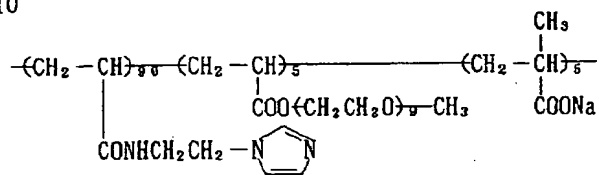
P - 9



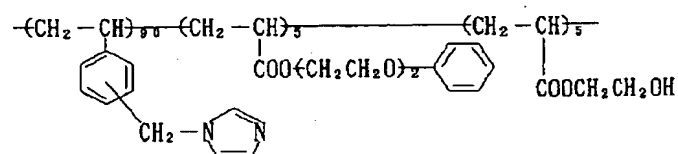
[0018]

[Chem. 8]

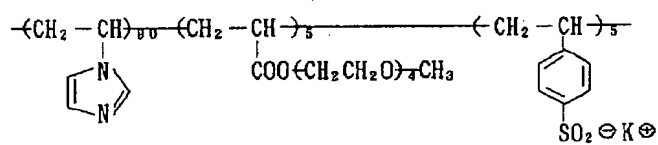
P-10



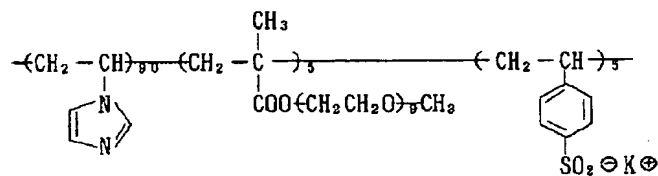
P-11



P-12



P-13



[0019]

[Chem. 9]

$$\begin{array}{c} \text{---}(\text{CH}_2\text{---}\underset{\text{N}}{\underset{\text{N}}{\text{C}}}\text{---})_{15}\text{---}(\text{CH}_2\text{---}\underset{\text{COOCH}_2\text{CH}_2\text{OC---CH}_2\text{CH}_2\text{CO---}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3}{\text{C}}\text{---})_6\text{---} \\ \text{N} \quad \text{N} \end{array}$$
$$\begin{array}{c} \text{---}(\text{CH}_2\text{---}\underset{\text{Pyridine ring}}{\text{CH}})\text{---}_y\text{---}(\text{CH}_2\text{---}\underset{\text{CONH(CH}_2\text{CH}_2\text{O)}_y\text{---CH}_3}{\text{CH}})\text{---}_z\text{---}(\text{CH}_2\text{---}\underset{\text{Phenyl ring with SO}_3^-\text{K}^+}{\text{CH}})\text{---}_x \\ \text{Pyridine ring} \quad \text{CONH(CH}_2\text{CH}_2\text{O)}_y\text{---CH}_3 \quad \text{Phenyl ring with SO}_3^-\text{K}^+ \end{array}$$
[illegible]
$$\text{-(CH}_2\text{-CH)}_{82.5}\text{-CH}_2\text{-CH}_2\text{-(CH}_2\text{-CH)}_{31.25}\text{-CH}_2\text{-CH}_2\text{-(CH}_2\text{-CH)}_{8.25}\text{-CH}_2\text{-CH}_2\text{-SO}_3^-\text{K}^+$$

[0021] In the present invention, by incorporating dye-receptive polymer represented by general formula (I) into a coating layer, the dye in the ink is firmly received, the image quality is raised and it is possible to markedly enhance the light fastness.

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trimethylsilyl groups or a silicone, etc. These are preferably employed as a colloidal-form silica (colloidal silica). The average particle size of the silica pigment used is preferably 4  $\mu$ -120  $\mu$ , and more preferably 4  $\mu$ -100  $\mu$ . Moreover, while the silica pigment employed in the present invention may or may not be porous, it is preferred that it be porous. The mean pore diameter in the silica pigment particles is preferably 50-500 Å and the pore volume is preferably 0.5-3 cc/g. The amount used is 20-50 g/m<sup>2</sup> and preferably 30-40 g/m<sup>2</sup>.

[0023] In the present invention, by incorporating the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment in the same coating layer, a structure is formed and the coating layer can be made porous, so that it is possible for the ink absorption rate to be made very rapid. As a result, the image quality is raised, and the problem of transfer of the ink to other paper laid thereon or to other objects is overcome.

[0024] The weight ratio of the incorporated dye-receptive polymer represented by general formula (I) to the one or more types of silica pigment is dye-receptive polymer/silica pigment = 1/99-30/70 (weight ratio), and preferably 5/95-20/80 (weight ratio). If the amount of the dye-receptive polymer represented by general formula (I) is greater than this, then the pore volume of the coating layer formed is markedly reduced and the ink absorption rate is lowered. The maximum pore volume of said coating layer is preferably 0.1 to 3 cc/g. On the other hand, if the amount of the dye-receptive polymer represented by general formula (I) is less than this,

then the dye-receptivity of the coating layer is impaired, the image quality is reduced, the light fastness is lowered and a deterioration in the film quality occurs.

[0025] The applied amount of the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment can readily be determined by those skilled in the art, in accordance with the amount of ink dye used and the type and composition of the dye-receptive polymer represented by general formula (I). However, 3-70 g/m<sup>2</sup> is preferred and 5-60 g/m<sup>2</sup> is most preferred.

[0026] In the present invention a binder is optionally employed in this coating layer. It is preferred that a hydrophilic binder be used. Examples thereof are described on pages 26-28 of JP-A-62-253159. Specifically, a transparent or translucent hydrophilic binder is preferred such as, for example, natural compounds like proteins, e.g. gelatin and gelatin derivatives, cellulose derivatives, starch, gum Arabic, dextran, pullulan or other such polysaccharides, and also polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylamide and other such synthetic high polymer compounds. Moreover, there can be used the highly absorbent polymers described in JP-A-62-245260, that is to say there may be used homopolymers comprising vinyl polymers with -COOM or -SO<sub>3</sub>M groups (where M is a hydrogen atom or an alkali metal), or copolymers formed between such vinyl monomers, or with other vinyl monomers (for example sodium methacrylate or ammonium methacrylate). Two or more types of binder may also be used in combination. The weight ratio of the



binder/(dye-absorbing polymer + inorganic pigment) lies in the range 0.1/99.9 to 80/20. If the amount of binder is more than this, then the dye-receptive strength is lowered, the pore volume is reduced and the light fastness and the ink absorption rate are impaired, which is undesirable.

[0027] In the present invention, the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment, plus optionally-employed binder, together with the optionally-employed additives described below, are dissolved or dispersed in a solvent in any proportions, and by application and drying thereof the coating layer of the present invention can be obtained. The solvent may be an aqueous system or an organic solvent system. Furthermore, the coating method is not particularly restricted and, for example, it is possible to use advantageously a method such as a die coater, roll coater, blade coater, bar coater, comma coater, gravure coater or the like. The drying temperature after coating is not particularly restricted and may be any temperature providing the substrate is not harmed. Depending on the drying conditions, cracks may be produced in the coating layer surface. Such cracks may or may not be present, and the size of the cracks is not particularly restricted. In the present invention, there is provided a coating layer where the dye-receptive polymer and the one or more types of silica pigment explained in detail above are present in the same layer. Of the two or more coating layers, this layer may be an upper layer (hereinafter referred to as the upper layer) or a lower layer (hereinafter referred

to as the lower layer) but it is preferred that it be the lower layer.

[0028] It is possible to further enhance the image quality and the light fastness by incorporating the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment in the lower layer, and incorporating dye-receptive polymer represented by general formula (I) in the upper layer or, alternatively, incorporating one or more types of inorganic pigment in the upper layer.

[0029] First of all, explanation is provided of the case where the dye-receptive polymer represented by general formula (I) and the one or more types of silica pigment are incorporated in the lower layer, and dye-receptive polymer represented by general formula (I) incorporated in the upper layer. With regard to the lower layer, there can be used, as it is, a layer obtained by the method described above.

[0030] The dye-receptive polymer represented by general formula (I) used in the upper layer is not particularly restricted and there can be used a compound of the kind described above. The amount of dye-receptive polymer represented by general formula (I) applied is preferably in the range 0.1 to 5 g/m<sup>2</sup>, and more preferably 0.2 to 4 g/m<sup>2</sup>. If there is less dye-receptive polymer represented by general formula (I) than this, then the dye-receptive strength of the coating layer is reduced and the light fastness is lowered. Optionally-employed binder is the same as described above. The binder/dye-receptive polymer weight ratio is from 30/70 to 95/5, and more preferably 40/60 to 90/10 by weight ratio. If

there is more binder than this, then the dye-receptive strength of the coating layer is reduced and the light fastness is lowered.

[0031] It is preferred that the water swelling factor of the upper layer as a whole be 100-300%, with 150-250% further preferred. Here, the swelling factor is the value obtained by dividing the swollen value when water has been dripped thereon, by the dry film thickness, and then multiplying by 100. As well as controlling the bleeding and spread of the ink, the swelling factor is also extremely important in terms of preventing damage within the printer, etc.

[0032] The upper layer coating method and the drying temperature are not particularly restricted, and there can be employed the same methods as above. Furthermore, there can be favourably employed a sequential application or simultaneous application method for the respective coating layers. By adopting this layer structure, since dye-receptive polymer represented by general formula (I) is incorporated in the upper layer, the image density is extremely high and the light fastness and image quality are outstanding. Moreover, since a porous layer is provided as the lower layer, the solvent and wetting agent in the ink are rapidly absorbed, and the ink drying rate is rapid. Next, explanation is provided of the case where dye-receptive polymer represented by general formula (I) and at least one type of silica pigment are incorporated in the lower layer and, furthermore, one or more types of inorganic pigment are incorporated in the upper layer. With regard to the lower layer, there can be used, as it is, the layer obtained by the method described above.

[0033] The inorganic pigments used in the upper layer are not especially restricted, but silica pigments or alumina pigments can be particularly favourably used. As silica pigments, there can be advantageously used those described above. As alumina pigments, there can be used either anhydrous alumina or alumina hydrates. As the anhydrous alumina, any of the alumina crystal forms  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -,  $\zeta$ -,  $\eta$ -,  $\theta$ -,  $\kappa$ -,  $\rho$ - and  $\chi$ - can be used. As alumina hydrates, there can be used the monohydrate or trihydrate. Examples of the monohydrate are pseudo-boehmite, boehmite and diaspora. Examples of the trihydrate are gibbsite and bayerite. Amongst these alumina pigments, alumina hydrate is preferably employed. The mean particle size of the alumina pigment used is preferably 4  $\mu$  to 300  $\mu$ , and more preferably 4  $\mu$  to 200  $\mu$ . Furthermore, the alumina pigment employed in the present invention may be porous or not but it is preferred that it be porous, and the average pore size in the alumina pigment particles is preferably 50-500  $\text{\AA}$ , while the pore volume is preferably 0.3-3 cc/g.

[0034] The method of synthesizing the alumina hydrate is not particularly restricted and, for example, there may be employed the sol-gel method in which ammonia is added to an aluminium salt solution and a precipitate produced, or the method of subjecting an alkali aluminate to hydrolysis. Furthermore, the product obtained by heating and dehydrating such materials may be used as an anhydrous alumina pigment. The applied amount of the inorganic pigment used is preferably 0.1 to 20 g/m<sup>2</sup> and more preferably 0.1 to 10 g/m<sup>2</sup>. This upper layer has the role of rapidly absorbing ink from the recording material surface into the interior, and if

the amount of applied inorganic pigment is more than enough for this then it becomes a cause of ink spread and bleeding in the horizontal direction of the recording material, so the image is impaired. On the other hand, if too little is used, then the ink absorption capacity is reduced and the ink absorption rate is lowered, beading is produced and the image is impaired.

[0035] The optionally-used binder is the same as that described above. The binder/inorganic pigment weight ratio is preferably 0.1/99.9 to 80/20, and more preferably 2/98 to 60/40 (weight ratio). With more binder than this, the pore volume of the upper layer is reduced and the ink absorption rate is markedly lowered, which is undesirable. The preferred pore volume of the upper layer is 0.1 to 3 cc/g. The method of applying this upper layer is not particularly restricted and there can be employed a method identical to that described above. Furthermore, for the respective layers there can be favourably employed either a simultaneous or sequential coating method. With such a layer structure, the ink absorption rate is extremely high and, furthermore, since the lower layer is a porous layer in which dye-receptive polymer represented by formula (I) is incorporated, the light fastness is excellent and the image quality outstanding.

[0036] Besides the aforesaid two coating layers, the inkjet image-recording medium of the present invention may optionally be provided with a protective layer, a layer with a fluorescent whitening agent for improvement of the white background, and a reinforcing layer such as a curl-preventing layer or the like. In particular, it

will be effective to provide a protective layer and a coating layer containing fluorescent whitening agent for improving the white background. It is also possible to use a matting agent in the inkjet image-recording medium of the present invention. As the matting agent, a conventionally-known such material can be used. Matting agents are well known in the photographic field and can be defined as being discontinuous solid particles of inorganic or organic materials which can be dispersed in a hydrophilic organic colloidal binder. Examples of inorganic matting agents are oxides (such as silicon dioxide, titanium oxide, magnesium oxide and aluminium oxide), alkaline earth metal salts (such as sulphates and carbonates, for example barium sulphate, calcium carbonate, magnesium sulphate and calcium carbonate {sic}), silver halide particles which do not form an image (silver chloride or silver bromide to which a trace of iodine atoms may be added as halogen component), and glass.

[0037] There can also be used the matting agents described in West German Patent 2,529,321, British Patent 760,775, British Patent 1,260,772, and US Patent Nos 1,201,905, 2,192,241, 3,053,662, 3,062,649, 3,257,206, 3,322,555, 3,353,958, 3,370,951, 3,411,907, 3,437,484, 3,523,022, 3,615,554, 3,635,714, 3,769,020, 4,021,245 and 4,029,504, etc.

[0038] Examples of organic matting agents include starch, cellulose esters (such as cellulose acetate propionate), cellulose ethers (such as ethyl cellulose), and synthetic resins. As examples of the synthetic resins, there are water-insoluble and sparingly water-soluble polymers such as polymers in which the monomer

components are alkyl (meth)acrylates, alkoxyalkyl (meth)acrylates, glycidyl (meth)acrylate, (meth)acrylamide, vinyl esters (such as vinyl acetate), acrylonitrile, olefins (such as ethylene), styrene, benzoguanamine, or formaldehyde condensates, on their own or in combinations thereof, or such monomer(s) in combination with acrylic acid, methacrylic acid,  $\alpha,\beta$ -unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylate, sulphoalkyl (meth)acrylate, styrenesulphonic acid or the like.

[0039] In addition, there can be used epoxy resins, nylon, polycarbonate, phenolic resins, polyvinyl carbazole, polyvinylidene chloride or the like. Moreover, there can be used the organic matting agents described in British Patent 1,055,713, and US Patent Nos 1,939,213, 2,221,873, 2,268,662, 2,322,037, 2,376,005, 2,391,181, 2,701,245, 2,992,101, 3,079,257, 3,262,782, 3,443,946, 3,516,832, 3,539,344, 3,591,379, 3,754,924 and 3,767,448, JP-A-49-106821 and JP-A-57-14835.

[0040] Amongst these, polymethyl methacrylate, benzoguanamine.formaldehyde condensed polymer (benzoguanamide resin, specifically that shown in the formula below {sic}; e.g. Epostar, commercial name of a Nippon Shokubai Co. product: chemical material 7-31, etc), polyolefin (such as Flowbeads LE-1080, CL-2080, HE-5023; commercial names of Nippon Steel Chemical Co. products; or Chemipearl V-100, commercial name of a Mitsui Petrochemical Industries product),

[0041] polystyrene beads (produced by the Moritex Corp.), nylon beads (produced by the Moritex Corp.), AS resin beads (produced by the Moritex Corp.), epoxy resin

beads (produced by the Moritex Corp.) and polycarbonate resin (produced by the Moritex Corp.) are preferred. As alkali-soluble matting agents, there can be used the alkyl methacrylate/methacrylic acid copolymers and the like described in JP-A-53-7231, JP-A-58-66937, JP-A-60-8894, or the alkali-soluble polymers containing anionic groups described in JP-A-58-166341. Combinations of such matting agents may also be used.

[0042] A hardener may also be utilized in the inkjet image-recording medium of the present invention. There are no particular restrictions on the hardener used in the recording medium of the present invention and known such materials may be employed. Examples include those of the aldehyde type (formaldehyde, glyoxal, glutaraldehyde, etc), aziridine type (as described in PB Report 19,921, US Patent Nos 2,950,197, 2,964,404, 2,983,611 and 3,271,175, JP-B-46-40898, JP-A-50-91315), isoxazole type (such as those described in US Patent 331,609), epoxy type (such as those described in US Patent 3,047,394, West German Patent 1,035,663, British Patent 1,033,518, JP-B-48-35495), vinyl sulphone type

[0043] (such as 1,3,5-triacryloyl-hexahydro-s-triazine, bis(vinylsulphonyl)methyl ether, N,N'-ethylene-bis(vinylsulphonylacetamido)ethane, N,N'-trimethylene-bis(vinylsulphonylacetamide) etc, and those described in PB Report 19,920, West German Patent Nos 1,100,942, 2,337,412, 2,545,722, 2,635,518, 2,742,308, 2,749,260, British Patent 1,251,091, Japanese Patent Application Nos 45-54236 and 48-110996, US Patent Nos 3,539,644 and 3,490,911), acryloyl type (for example those described in Japanese Patent Application No. 48-27949 and US



Patent 3,640,720), carbodiimide type (such as for example those described in

[0044] US Patent Nos 2,938,892, 4,043,818 and 4,061,499, JP-B-46-38715, Japanese Patent Application No. 49-15095), triazine type (such as 2,4-dichloro-6-hydroxy-s-triazine or the like, and those described in for example West German Patents 2,410,973 and 2,553,915, US Patent 3,325,287 and JP-A-52-12722), N-methylol type (dimethylolurea, methylol dimethylhydantoin, etc), dioxane derivatives (such as 2,3-dihydroxydioxane), mucohalogenic acid type (such as mucochloric acid and mucophenoxychloric acid), dialdehyde starch, 1-chloro-6-hydroxytriazine-modified gelatin, maleimide type, acetylene type and methanesulphonic acid ester type hardeners.

[0045] Furthermore, as examples of polymeric hardeners, there are the polymers with aldehyde groups described in US Patent 3,396,029 (such as acrolein copolymer), the polymers with dichlorotriazine groups described in US Patent 3,362,827 and Research Disclosure 17,333 (1978), the polymers with epoxy groups described in US Patent 3,623,878, polymers containing active vinyl groups or with precursor groups thereof, as described in Research Disclosure 16,725 (1978), US Patent 4,161,407, JP-A-54-65033 and JP-A-56-142524, and polymers with active ester groups as described in JP-A-56-66841. Any amount of hardener may be added but the amount will be appropriately about 0.1 to 30 wt% and in particular 0.5 to 10 wt% of the materials which can react therewith.

[0046] In the present invention, in order to prevent putrefaction of the liquid dispersion of the various

chemical agents or of the coating liquid, a bactericide/fungicide can be employed in the inkjet image-recording medium. Any water-soluble bactericide/fungicide can be used in the present invention, specific examples of which are thiazolylbenzimidazole compounds, isothiazolone compounds, chlorophenol compounds, bromophenol compounds, thiocyanic acid and isothiocyanic acid compounds, acid-azide compounds, diazine and triazine compounds, thiourea compounds, alkylguanidine compounds, quaternary ammonium salts, organo-tin and organo-zinc compounds, cyclohexylphenol compounds, imidazole and benzimidazole compounds, sulphamide compounds, chlorinated isocyanuric acid, active halogen compounds of sodium or the like, chelating agents, sulphurous acid compounds, antibiotics such as penicillin, and other such bactericides or fungicides. There can also be used the bactericides described by L.E. West in "Water Quality Criteria", Phot. Sci. and Eng. Vol.9, No.6 (1965); the various antifungal agents described in JP-A-57-8542, JP-A-58-105145, JP-A-59-126,533, JP-A-55-111,942 and JP-A-57-157244; and the bactericides/fungicides described by Hiroshi Horiguchi in "Bactericidal/Fungicidal Chemistry {Bokin Bokabi no Kagaku}" (published by Sankyo Shuppan in 1982).

[0047] Various types of surfactant may also be included in the inkjet image-recording medium of the present invention as a coating aid, antistatic agent, slip improver, adhesion preventive or for other purposes. For example, there can be used non-ionic surfactants like saponin (steroid system), alkylene oxide derivatives (such as polyethylene glycol, polyethylene glycol/polypropylene glycol condensate, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl

ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or amides, and polyethylene oxide adducts of silicones), glycidol {sic} derivatives (such as polyglyceride alkenylsuccinate and alkylphenol polyglyceride) and alkyl esters such as the fatty acid esters of polyhydric alcohols; anionic surfactants which have an acidic group such as a carboxy group, sulpho group, phospho group, sulphate ester group or phosphate ester group, like alkylcarboxylates, alkylsulphonates, alkylbenzenesulphonates, alkyl-naphthalenesulphonates, alkylsulphate esters, alkylphosphate esters, N-acyl-N-alkyltauric acid, sulphosuccinate esters, phosphoalkyl<sup>1</sup> polyoxyethylene alkylphenyl ethers and polyoxyethylene alkyl eicosanoic acid esters; amphoteric surfactants such as amino acids, aminoalkyl sulphonic acids, aminoalkyl sulphate esters or phosphate esters, alkyl-betaines and amine oxides; and cationic surfactants such as alkylamine salts, aliphatic or aromatic quaternary ammonium salts, pyridinium, imidazolium or other such heterocyclic quaternary ammonium salts, and aliphatic or heterocycle-containing phosphonium or sulphonium salts, etc.

[0048] It is possible to use high-boiling organic solvents as plasticizers, slip agents or curl preventives in the inkjet image-recording medium of the present invention. Specifically, there are those described in the aforesaid Research Disclosure and JP-A-62-245,253, etc. Furthermore, there may be employed for such purposes various kinds of silicone oils (of all types ranging from dimethyl silicone oil to modified silicone oils where various organic groups are introduced into the dimethylsiloxane). Effective examples thereof are the various modified silicone oils

described in "Modified Silicone Oil", technical data P6-18B published by the Shin-Etsu Silicone Co., in particular carboxy-modified silicone (commercial name X-22-3710). Furthermore, the silicone oils described in JP-A-62-215,953 and JP-A-63-46,449 are also effective.

[0049] Fluorescent whitening agents may also be used in the image-recording medium of the present invention. In particular, it is preferred that the fluorescent whitening agent either be incorporated in the recording medium or that it be supplied to the recording medium from outside by being contained in the ink for example. Examples of the fluorescent whitening agents are the compounds described in chapter 8 of volume V of "The Chemistry of Synthetic Dyes" by K. Venkataraman (Ed.) or in JP-A-61-143752. More specifically, there are stilbene compounds, coumarin compounds, biphenyl compounds, benzoxazolyl compounds, naphthalimide compounds, pyrazoline compounds and carbostyryl compounds. The fluorescent whitening agents can be used in combination with a fading inhibitor.

[0050] There are no particular restrictions on the substrate in the inkjet image-recording medium in the present invention, and examples include paper and synthetic polymer (film). Specific examples are polyethylene terephthalate, polycarbonate, polyvinyl chloride, polystyrene, polypropylene, polyimide and celluloses (such as triacetyl cellulose), or a film of these in which a pigment such as titanium oxide has been incorporated, and also film-method synthetic paper produced from polypropylene or the like, a mixed-pulp paper produced from natural pulp and a synthetic resin pulp such as polyethylene, Yankee paper, baryta paper,

cast-coat paper, metal, cloth and glass. These may be employed on their own or there can be used a substrate produced by the lamination, to one or both faces, of a synthetic polymer such as polyethylene. It is also possible to use the substrates described in JP-A-62-253159.

[0051] Particularly preferred substrates in the present invention are paper or plastic substrates, laminated on both sides with a polyolefin (for example polyethylene, polystyrene or polybutene) or with polyethylene terephthalate (however, it is preferred that a white pigment such as titanium dioxide or zinc oxide, or a blue toning pigment such as cobalt blue, ultramarine or neodymium oxide be incorporated into the polyolefin).

[0052] With regard to the thickness of the polyolefin layer(s), this is not particularly restricted but from 10 to 100  $\mu\text{m}$  is preferred, in particular from 15 to 50  $\mu\text{m}$ , and especially 20 to 35  $\mu\text{m}$ . The surface state of the polyolefin may be of any kind, for example it may be a mirror surface, or it may be provided with regular or irregular projections and indentations, but it is preferred that the face side has a mirror finish. The surface of the polyolefin layer is subjected to a surface-activating treatment such as a corona discharge treatment or a flame treatment, and an undercoat layer may optionally be provided, with the coating layers of the present invention applied on top. There are no particular restrictions on the white pigment which can be incorporated in the polyolefin of the face side, but titanium oxide or zinc oxide is preferred. Anatase type titanium oxide is particularly preferred, and in order to enhance the dispersion properties it is preferred

that there be jointly employed up to 50% of zinc oxide. The amount of white pigment incorporated in the polyolefin is preferably at least 5 wt%, more preferably 10-50 wt% and in particular 15-30%.

[0053] There are no particular restrictions on the toning pigment which can be incorporated into the polyolefin on the face side, but one which can withstand a coating temperature of 300°C or more is preferred such as cobalt blue, ultramarine or neodymium oxide. The amount of toning pigment used is 0.1 to 3 wt% in terms of the white pigment. In order to realize the surface reflection characteristics which are the aim of the present invention, the selection of the toning pigment and the amount used is particularly important. Pigments described as ultramarine differ widely in colour shade between manufacturers and lot numbers, so it is preferred that various pigments be used as a blend to achieve the surface reflection characteristics of the present invention.

[0054] In the case where the substrate is paper laminated with polyethylene in which a white pigment such as titanium oxide has been incorporated, the back layer is designed to have an antistatic function and the surface resistivity will be no more than  $10^{12} \Omega \cdot \text{cm}$ .

[0055] The inkjet image-recording medium of the present invention can be used in all systems comprising dye discharge and reception, including inkjet printing, sublimation type thermal transfer printing and dye-diffusion transfer printing. In particular, when used in inkjet printing, the effects of the present invention are markedly manifested.

[0056] There are absolutely no restrictions on the inkjet printing system, and the recording medium of the present invention can be used irrespective of whether it is a continuous system or an on-demand system. Furthermore, there are no restrictions on the inkjet head type, and any printer type may be employed including the piezo type, bubble-jet type, thermal-jet type and type employing ultrasonic waves.

[0057] Recent advances in inkjet systems have been remarkable, and numerous novel systems have been proposed and put into practice, such as the system where ink of low concentration known as photoink is discharged as a multitude of small-volume droplets, the system where the image quality is improved using a plurality of inks of substantially the same hue but different concentrations, and the system using colourless transparent inks. The recording medium of the present invention is advantageously used in all of these but, in particular, the image quality improvement effects are markedly manifested with a printer of high printing rate or with a printer based on a system where ink of low concentration is discharged in large amounts.

[0058]

[Examples] Below, the present invention is explained by providing examples.

#### Example 1

By means of the extrusion coating method, polyethylene was laminated at 300°C to both faces of a high quality

paper (density 1.053, thickness 152  $\mu\text{m}$ ) of pulp mixing ratio of LBKP/NBSP = 6/4, so that a substrate was prepared. On the bottom face there was used high density polyethylene of density 0.955 and on the top face there was used polyethylene of density 0.923 in which were mixed surface-treated titanium as a white pigment and ultramarine (bluish and reddish; produced by the Daiichi Kasei Co.) as a toning pigment. The top polyethylene thickness was 36  $\mu\text{m}$  and the bottom polyethylene thickness was 27  $\mu\text{m}$ . Two coating layers were then applied in succession onto this resin-covered substrate such that the solids contents after drying were as shown below, and an image-recording medium material thus produced.

[0059]

(Lower layer)

Compound P-17	3.0 g/m <sup>2</sup>
Cataloid-SI80P	35.0 g/m <sup>2</sup>
(colloidal silica produced by the Catalysts & Chemicals Industries Co. Ltd)	

(Upper layer)

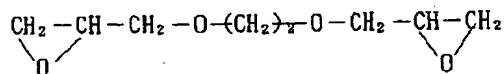
PVA435	3.0 g/m <sup>2</sup>
(polyvinyl alcohol produced by the Kuraray Co.)	
Compound P-17	1.0 g/m <sup>2</sup>
Compound H-01 (hardener)	0.01 g/m <sup>2</sup>
Compound W-01 (surfactant)	0.1 g/m <sup>2</sup>

[0060]

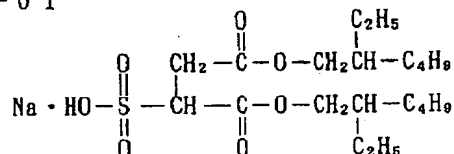
[Chem. 10]



H-01



W-01



[0061] Evaluation was then carried out of this image-recording medium sample using the methods described below. The image quality was evaluated based on the image density, beading (granular variations in density) and bleeding. Printing was carried out in every case using a model PM700C Inkjet Printer (produced by Epson).

[0062] <Ink Drying Time> Solid printing was carried out with yellow (Y), magenta (M), cyan (C) and black (Bk) printing inks and, after printing, the time was measured for the inks to be fixed and dried to the touch.

- ⊙ dries within 1 second
- O dries within 10 seconds
- Δ dries within 1 minute
- X dries within 10 minutes
- XX dries in more than 10 minutes

<Image Density> Solid printing was carried out with the M ink, and then the image density measured using a reflection densitometer (X-Rite 310TR).

<Beading> Solid printing was carried out with the Y, M, C and Bk inks, and then granular density variations evaluated by eye.

- O no granular density variations
- Δ some granular density variations noted
- X many granular density variations noted

<Bleeding> Solid printing was carried out with the Y, M, C and Bk inks, and then the occurrence of bleeding evaluated by eye.

- O no bleeding noted
- Δ some bleeding noted
- X considerable bleeding noted

<Light Fastness> Solid printing was carried out with the M ink, and then the sample was subjected to 1 week of irradiation with xenon light (85,000 lux) using an Atlas Ci-65 weatherometer. The image densities before and after the xenon light irradiation were measured using the aforesaid reflection densitometer, and the light fastness of the image was evaluated from the percentage dye remaining. The percentage dye remaining was determined from the following relationship.

$$\text{percentage dye remaining} = (\text{image density after xenon light irradiation}) / (\text{image density after } \{sic\} \text{ xenon light irradiation}) \times 100 (\%)$$

The results of the evaluations are shown in Table 1.

[0063]

[Table 1]

Example	Ink Drying Time	Image Density	Beading	Bleeding	Light Fastness (%)
Example 1	O	1.80	O	O	95
Example 2	O	1.80	O	O	92
Example 3	O	1.75	O	O	90
Example 4	O	1.72	O	O	90
Example 5	⊙	1.70	O	O	90
Example 6	⊙	1.70	O	O	89
Example 7	⊙	1.68	O	O	88
Example 8	⊙	1.67	O	O	89
Comp.Ex.1	XX	1.80	X	Δ	93
Comp.Ex.2	XX	1.27	Δ	X	25

[0064] Examples 2 to 4

Image-recording medium samples were prepared in the same way as in Example 1 except that the dye-receptive polymer compound P-17 in the upper layer in Example 1 was replaced by the following dye-receptive polymers respectively, and then evaluation was carried out by the same methods as in Example 1. The evaluation results are shown in Table 1.

Example 2            P-1  
 Example 3            P-5  
 Example 4            P-10

[0065] Example 5

An image-recording medium sample was prepared by the same method as in Example 1, with the sequential application of the two coating layers being carried out such that the solids contents after drying were as follows.

[0066]

(Lower layer)

Compound P-17	3.0 g/m <sup>2</sup>
Cataloid-SI80P (colloidal silica produced by the Catalysts & Chemicals Industries Co. Ltd)	35.0 g/m <sup>2</sup>

(Upper layer)

PVA440 (polyvinyl alcohol produced by the Kuraray Co.)	0.5 g/m <sup>2</sup>
A-300 (silica produced by the Nippon Aerosil Co.)	0.5 g/m <sup>2</sup>
Compound W-01 (surfactant)	0.01 g/m <sup>2</sup>

The evaluation of this image-recording medium sample was carried out by the same methods as in Example 1 and the evaluation results are shown in Table 1.

[0067] Examples 6-8

Image-recording medium samples were prepared by the same method as in Example 5 except that the following dye-receptive polymers were respectively used instead of the dye-receptive polymer Compound P-17 in the lower layer in Example 5, and then evaluation was carried out by the same methods as in Example 1. The evaluation results are shown in Table 1.

Example 2 {sic}	P-1
Example 3 {sic}	P-5
Example 4 {sic}	P-10

[0068] Example 9

An image-recording medium sample was prepared by the same method as in Example 1, with the sequential application of the two coating layers being carried out such that the solids component contents after drying were as follows.

[0069]

(Lower layer)

Compound P-17	3.0 g/m <sup>2</sup>
Cataloid-SI80P (colloidal silica produced by the Catalysts & Chemicals Industries Co. Ltd)	35.0 g/m <sup>2</sup>

(Upper layer)

PVA124 (polyvinyl alcohol produced by the Kuraray Co.)	0.2 g/m <sup>2</sup>
Cataloid-AS3 (pseudo-boehmite alumina hydrate pigment produced by the Catalysts & Chemicals Industries Co. Ltd)	0.8 g/m <sup>2</sup>
Compound W-01 (surfactant)	0.01 g/m <sup>2</sup>

The evaluation of this image-recording medium sample was carried out by the same methods as in Example 1 and the evaluation results are shown in Table 1.

[0070] Comparative Example 1

An image-recording medium sample was prepared by providing, on the resin coated substrate produced in Example 1, a coating layer with the following solids content after drying.

[0071]

Compound P-17 (dye-receptive polymer)	5.0 g/m <sup>2</sup>
PVA420 (binding agent, polyvinyl alcohol produced by the Kuraray Co.)	3.5 g/m <sup>2</sup>

Compound H-01 (hardener)

0.08 g/m<sup>2</sup>

Compound W-01 (surfactant)

0.02 g/m<sup>2</sup>

The evaluation of this image-recording material was carried out by the same methods as in Example 1 and the evaluation results are shown in Table 1.

[0072] Comparative Example 2

An image-recording medium sample was produced by the same method as in Example 1 except that instead of the dye-receptive polymer Compound P-17 there was used polyvinyl pyrrolidone, and then evaluation was carried out by the same method as in Example 1. The evaluation results are shown in Table 1.

[0073]

[Effects of the Invention] It is clear that the inkjet image-recording medium of the present invention has a rapid ink drying rate, and has excellent image quality and outstanding light fastness.

*Translator's note*

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<sup>i</sup> There is a spelling mistake in the Japanese here and it is not clear what compound was meant. It may be sulphoalkyl or phosphoalkyl.